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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The following thermoplastic elastomers (TPE) have been synthesized, characterized, and some of them submitted to DOD laboratories for evaluation: multiblock poly(acetal) poly(urethanes), where the poly(acetals) are poly(1,3,6trioxocane derivatives) and (1,3-dioxepane deriatives), triblock TPE of poly(acetal) and poly(dioxolane-co-trioxane) hard termini, liquid crystalline TPE's, chain-end interactive TPE, and Energetic multiblock and triblock TPE's using BAMO as the hard segment and AMMO or NMMO as soft segments.

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Final Technical Report

for

ONR Contract N00014-85-k-0880

Submitted by

James C. W. Chien, Department of Polymer Science and Engineering, Department of Chemistry, University of Massachusetts, Amherst, MA 01003

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Objectives

To initiate new concepts for thermoplastic elastomers (TPE) as propellent binders, to demonstrate the feasibility of concepts, to prepare samples for evaluation, and to submit the samples to laboratories designated by ONR.

Phase I Synthesis of Segmented TPE from Available Building Blocks and Characterization

Telechilic polyethers (α, ω-dihydroxy poly(tetrahydrofuran) MW = 420, 1,000, 2,000, 3,000, 4,000) were chain extended and coupled with MDI and TDI into segmented TPE's. Relationships of thermal, mechanical, rheological and other poperties with structures of TPE were found.

1. Thermal Degradation Studies of Segmented Thermoplastic Elastomers, J. L. Fan and J. C. W. Chien, *Polym. Degrad. Stab.* **12** 43-63 (1985).

2. Structure-Property Relationships in Thermoplastic Elastomers, I. Segmented Polyether-polyurethanes, E. J. Woo, G. Farber, R. Farris, C. P. Lillya and J. C. W. Chien, *Polym. Sci. Eng.* **25** 834-840 (1985).

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3. Structure-Property Relationships in Thermoplastic Elastomers, III. Segmented Polyacetal-Polyurethanes, B. Xu, D. N. Khanna, C. P. Lillya and J. C. W. Chien, *J. Appl. Polym. Sci.* **31** 123 (1986).

4. Relaxation Properties of Some Segmented Polyurethane - $CaCO_3$ Composites. A Dielectric Study, G. Banhegyi, M. K. Rho, J. C. W. Chien and F. E. Karasz, *J. Polym. Sci. Polym. Phys. Ed.* **25** 57-69 (1987).

5. Structure-Property Relationships in Thermoplastic Elastomers, IV. Dynamic Mechanical Relaxations in Poly(dioxolane), Poly(butyltrioxocane) and Poly(propylene oxide) Polyurethanes, J. C. W. Chien and M. K. Rho, *J. Appl. Polym. Sci.* **36** 1387-1400 (1988).

6. Efficient Synthesis of the Triblock Copolymer Styrene-*b*-tetrahydrofuran-*b*-Styrene by Coupling of Pre-formed Blocks, J. C. W. Chien, J. L. Hong and C. P. Lillya, *Appl. Polym. Sci.* **41** 775-785 (1990).

Phase II Synthesis of Novel Acid Depolymerizable Soft Block for Low Vulnerability TPE

We developed new methods to obtain α, ω-dihydroxy polyacetals which possesses very low T_g and acid depolymerizibility at > 200°C as building blocks for low vulnerability TPE binders. The novel materials are:

α, ω-dihydroxy poly(1,3,6-trioxocane)
α, ω-dihydroxy poly(2-butyl-1,3,6-trioxocane)
α, ω-dihydroxy poly(dioxepane)
α, ω-dihydroxy poly(2-butyl-dioxepane)

These polymerizations have been published.

7. Cationic Polymerizations of 1,3,6-Trioxocane and 2-Butyl-1,3,6-Trioxocane, B. Xu, C. P. Lillya and J. C. W. Chien, *Macromolecules* **20** 1445-1450 (1987).

8. Cationic Polymerizations of Dioxepane and Its' 2-Alkyl Derivatives, J. C. W. Chien, Y. G. Cheun and C. P. Lillya, *Macromolecules* **21** 870-875 (1988).

9. Cationic Copolymerizations of Cyclooxaalkanes, Y. G. Cheun, C. P. Lillya, P. H. Lahti and J. C. W. Chien, *Macromolecules* **23** 59-65 (1990).

10. An AM1 Computational Study of the Catioric Polymerization Mechanism of Cyclic Acetals, P.M. Lahti, C.P. Lillya and J.C.W. Chien, *Macromolecules,* **22,** 1214-1218 (1990)

Phase III Synthesis of Novel Acid Depolymerizable Crystalline Block for Low Vulnerability TPE

The hard segments for low vulnerability TPE binders must possess temperature of melting in the vicinity of 100°C for easy and safe processing and no loss of mechanical properties for storage under desert conditions. We achieved the synthesis of the following new materials:

α, ω-dihydroxy poly(dioxolane-co-trioxane)
α, ω-dihydroxy poly(dioxolane-co-trioxane)

The rheological properties of the TPE had been investigated.

11. Effect of Shear Stress on Viscoelastic Properties of a Phase-Separated Multi-block Copolymer, Y. G. Lin, P. W. Jin, J. C. W. Chien and H. H. Winter *Polymer* **30** 831-834 (1989).

Segmented and linear triblock low vulnerability TPE's were assembled from the above hard and soft segments and samples submitted to United Technology, Morton Thiokol and Army Ballistics Laboratories.

Phase IV Liquid Crystalline TPE

We invented the concept that by the introduction of short mesogenic entities at the termini of flexible segments, mesophase forming TPE may be obtained. This concept was demonstrated by the synthesis of liquid crystalline twin macromolecules and studied their rheological behaviors.

12. Versatile Synthesis of Liquid Crystalline Thermoplastic Elastomers, J. C. W. Chien,*SPIE Transaction* **872** 92-95 (1988).

13. Rheology of a Twin Liquid Crystalline Polymer, Y. G. Lin, R. Zhou, J. C. W. Chien and H. H. Winter, *Macromolecules* **21** 2014-2018 (1988).

14. Structure and Rheology of Twin Liquid Crystalline Polymers, Y. G.Lin, R. Zhou, J. C. W. Chien and H. H. Winter, *Polymer* **30** 2204-2208 (1989).

Phase V TPE with Associative Termini

The triblock TPE is usually interior in physical and mechanical properties than multisegmented TPE because of the lower molecular weight of the former. We conceived the idea that if the termini of a triblock TPE are associated at use-temperature and dissociated at processing temperatures, then it will have good mechanical properties because of the high effective molecular weight due to linear chain extension by association and also good processing behaviors because of the low effective molecular weight when the associations are disrupted. This concept has been proven.

15. Linear Chain Extension Through Associative Termini, C.P. Lillya, R. Baker, H.H. Winter, G.-Y. Lin, J. Shi, L.C. Dickinson, and J.C.W. Chien, *Macromolecules,* submitted.

Phase VI Synthesis of energetic polyoxetanes with spirobenzoxasilole

Sequential polymerization of energetic oxetanes by acid catalysis had not been successful. A new catalyst, spirobenzoxasilole had come to our attention. We thought it might be possible to use this catalyst to synthesize telechilic polymers of energetic oxetanes: BAMO (bisazidomethyloxetane), AMMO (azidomethyl-methyloxetane), NMMO (nitratomethyl-methyloxetane), and BEMO (bisethoxy-methyloxetane). The poly(BAMO) will be used as the terminal hard segments whereas any of the other three can be useful as the middle soft segment.

We have succeeded in the synthesis of the following new building blocks:

α-hydroxy poly(BAMO)
α, ω-dihydroxy poly(BAMO)
α, ω-dihydroxy poly(AMMO)
α, ω-dihydroxy poly(NMMO)
α, ω-dihydroxy poly(BEMO)

16. Spinobenzoxasilole catalyzed polymerization of Oxetane Derivatives, B. Xu, C. P. Lillya, and J. C. W. Chien, *J. Polym. Sci. Part A*, submitted.

17. Synthesis and Characterization of Energetic Thermoplastic Elastomers, B. Xu, C. P. Lillay, and J. C. W. Chien, *J. Polym. Sci. Part A*, submitted.

Samples of linear triblock poly(BAMO-*CO*-AMMO-*CO*-BAMO) and poly(BAMO-*CO*-NMMO-*CO*-BAMO) have been submitted to China Lake for evaluation.

Thesis

I. "Nitration of Diene Polymers"
Bing-Hwei Douglas Su, Ph.D. (1983).

II. "Synthesis of Azido-Polymers of Butadiene"
Rong-Hwei Juang, M.S. (1984).

III. "Nitromercuratron of Olefins, Suppression of By-Product Formation and Extension to Water-Insoluble Olefins"
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V. "The Synthesis and Characterization of Block Copolymers"
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VII. "Synthesis and Characterization of Polyacetals and Their Urethane Copolymers"
Dong-Tsai Hseih, Ph.D. (1988).

VIII. "Liquid Crystalline Segmented and Triblock Copolymers"
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IX. "Transition Metal Containing Conducting Polymers and Segmented Carborane Based Polyether Triblock Copolymers"
Huey Huey Lo, Ph.D. (1990).

Final Patent Report

for

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Submitted by

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Two Disclosures of Invention:

(1) Synthesis of low vulnerability thermoplastic elastomers.

(2) Synthesis of liquid crystalline thermoplastic elastomers.

were submitted to ONR. No patent action was taken.